VI.13 A High Temperature Electrochemical Energy Storage System Based on Sodium Beta Alumina Solid Electrolyte (BASE)

Objectives

Phase I

- To synthesize planar, thin, strong BASE using a patented vapor phase process.
- To fabricate metal end caps and the associated hardware for the construction of planar BASE-based electrochemical energy storage systems.
- To construct electrochemical cells comprising of a sodium anode, BASE, and selected cathodes.
- To electrochemically test cells (discharge-charge) over a range of temperatures and up to the highest possible depths of discharge.
- To conduct theoretical analysis of the electrochemical energy storage system from the standpoint of maximum possible capacity, efficiency, and integrability with power generation systems.

Phase II

- To construct a planar stack of ten Na/BASE/optimized cathode cells.
- To operate a stack for a minimum of 100 charge-discharge cycles.
- To thermally cycle the stack between the operating temperature and room temperature.
- To disassemble the stack and conduct post mortem analysis.

Approach

- Fabricate BASE discs by the method of die pressing or tape casting and BASE tubes by the method of slip casting using a vapor phase process.
- Measure the conductivity of BASE tubes by assembling a symmetric cell with zinc chloride – sodium chloride eutectic mixture.
- Construct tubular electrochemical cells that could be assembled in three different states: discharged state, charged state, and partially charged at eutectic composition.
- Conduct experiments to test the electrochemical working of tubular cells and to analyze the voltage response of the charge-discharge cycles.
- Construct planar cells and to test the electrochemical working of the same by analyzing the voltage response of the charge-discharge cycles.
- Conduct several freeze-thaw cycles on the planar cells and test the performance of the same after undergoing thermal cycles.
- Test the stability of BASE as electrolyte with zinc chloride as the cathode.

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Accomplishments

- BASE discs were successfully fabricated by tape casting, sintering and vapor phase treatment.
- BASE tubes were successfully fabricated by slip casting, sintering and vapor phase treatment.
- BASE was shown to be stable in aqueous media (no $NaAlO_2$ at grain boundaries).
- Electrochemical cells were designed, constructed, and tested.
- No incorporation of zinc within the BASE structure was observed, suggesting that BASE is stable in the battery environment.
- A tubular electrochemical cell with a zinc chloride cathode was successfully discharged at 2 V.
- Planar cells were designed and assembled.
- Freeze-thawing of planar cells was done a couple of times followed by several charge-discharge cycles without failure of the electrolyte. These tests were conducted at an operating temperature of 350°C.

Future Directions

- Assemble a planar stack of five Na/BASE/$ZnCl_2$ cells and test the electrochemical working of the cell stack.
- Construct and test electrochemical cells comprising of a sodium anode, BASE, and alternative cathodes.
- Integration of the high temperature energy storage system based on BASE with a power generation system.

Introduction

The demand for electricity varies depending upon the time of the day: low demand during night and high demand during day. All power plants are designed for peak power which leads to the underutilization of excess capacity during off peak periods. One of the main reasons for the emergence of electrochemical energy storage devices, such as batteries, is that power plants can be designed for average demand. This will augment the capacity of power plants as the excess energy during off peak periods will be stored for use later during high peak demands. This strategy is expected to lower capital costs.

Sodium beta" alumina solid electrolyte, commonly referred to as BASE, is an excellent conductor of sodium ions at 300°C. This cell has liquid sodium as the anode, BASE as the electrolyte and liquid $ZnCl_2$ as the cathode. During charging and discharging, sodium ions pass through the BASE electrolyte from cathode to anode and anode to cathode, respectively. The current applications of this solid electrolyte include the Na-S battery, the Zebra battery and the sodium heat engine. The Na-S battery has a demonstrated life of greater than 7 years in a 500 kW size. This shows that BASE has outstanding stability in rather corrosive environments – far superior than any other solid electrolyte being considered for active electrochemical devices. Work to date shows that BASE is the only known solid electrolyte with such a wide range of applicability (from as low as ~ 100°C to over 1,000°C), and excellent stability in strongly reducing and oxidizing environments.

Approach

BASE discs were fabricated using the method of tape casting of alumina + zirconia followed by vapor phase conversion (Figure 1). The dispersant used was KD1. BASE tubes were fabricated by the method of slip casting with Darvan C as the deflocculent. The conductivity of BASE tubes was measured by assembling symmetric cells. A eutectic mixture of NaCl-$ZnCl_2$ was used as both the electrodes in the symmetrical cell. The cell was then cycled at constant current mode supplying 500 mA for 50 hours. The operating temperature was 350°C. A few BASE samples were put in an aqueous solution of NaOH (40(w/v) %) and boiled for 5 hours. This test was conducted to make sure that the samples would survive in a basic aqueous environment. The x-ray diffraction patterns and microstructures of the samples after treating with NaOH were taken and analyzed. Experiments were conducted to test the electrochemical working of the tubular cells assembled in the discharged state, charged state and partially charged state at eutectic composition. Planar cells were designed and assembled using the tape cast BASE discs. The working of planar cells was tested at the constant current mode and the cells were thermally cycled between the operating temperature and room temperature. The performance of the planar cells was monitored after several freeze-thaw cycles. An experiment was conducted to test the stability of BASE in a zinc chloride environment. BASE tubes were soaked in molten zinc chloride at a temperature of 430°C for 22 hours. The samples were weighed before and after the treatment with $ZnCl_2$. Then, the samples were analyzed using scanning electron microscopy (SEM). Chemical line scan was done on the samples using SEM for analyzing the composition of the samples. The next step is to design and assemble a planar stack of five cells.

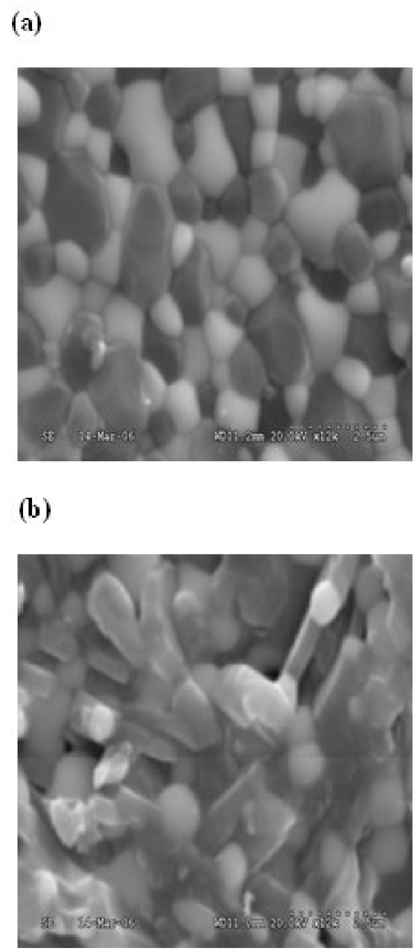

FIGURE 1. Microstructures of (a) As-Sintered Tape Cast Sample and (b) BASE Tape after Vapor Phase Conversion

Results

1. The voltage response of the symmetrical cell was analyzed. There was no evidence of an increase in resistance with time. From the values of voltage and current obtained from the experiment, the resistance of the overall cell was calculated to be 0.15 Ω. This includes the resistance of the BASE tube, molten salts and the polarization resistance.
2. The x-ray diffraction pattern of the sample which was treated with NaOH solution was analyzed. The analysis of peaks showed no difference from the BASE before treating with NaOH solution. There was no significant difference in the surface of the samples other than the sample was slightly etched.
3. A number of tubular cells were assembled and tested to study the electrochemical working at an operating temperature of 350°C. The analyses of the voltage response of the cells showed a fairly constant discharge voltage of about 2.0 V when operated under the constant current mode (Figure 2). The last cell assembled in the fully charged state was discharged for about 20 hours with a constant discharge voltage of 1.9 V.
4. A planar cell was assembled in the partially discharged state at eutectic composition (Figure 3). Voltage responses of the charge-discharge cycles of the planar cells were analyzed (Figure 4). The cell was operated for about 2 hours after each freeze-thaw cycle (Figure 5). The open circuit voltage obtained was about 2.35 V. The cell was operated at a constant current of 100 mA and at a temperature of 350°C.
5. Stability of BASE in a $ZnCl_2$ environment was tested by soaking BASE samples in molten zinc chloride. The samples were weighed before and after the experiment and no change in weight was observed.

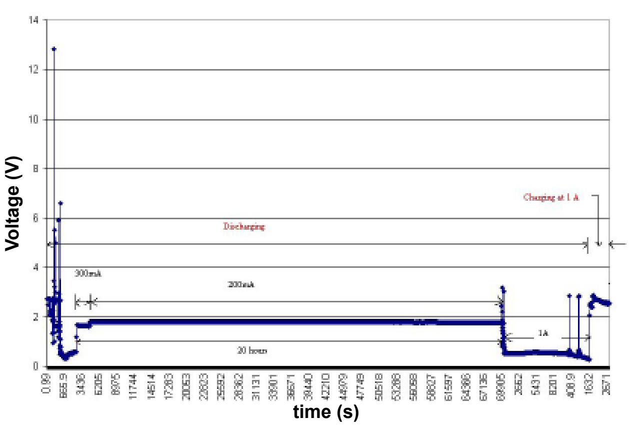

FIGURE 2. Voltage response of the discharging and charging of tubular cell assembled in the fully charged state. This shows that a tubular cell can be successfully discharged and charged.

FIGURE 3. Assembled View of the Planar Cell

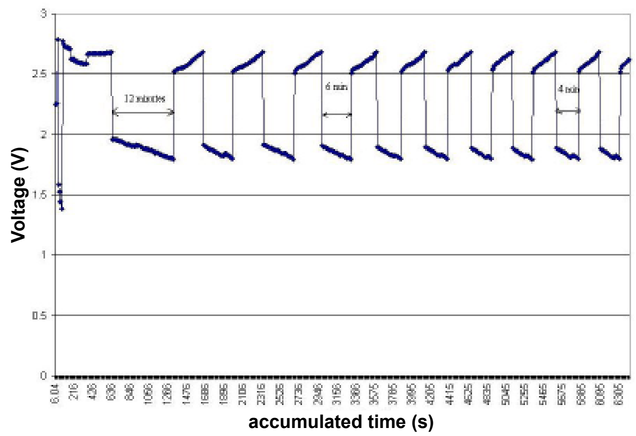

FIGURE 4. Voltage response of the charging and discharging of the planar cell assembled in the partially charged state. This shows that a planar cell could be subjected to repeated charge-discharge cycles.

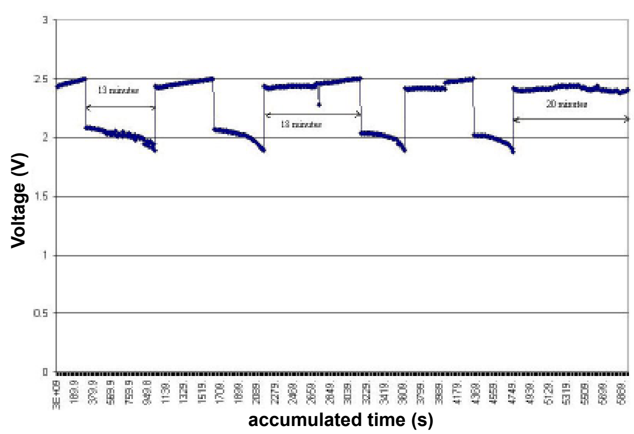

FIGURE 5. Voltage Response of the Charging and Discharging of the Planar Cell after Two Freeze-Thaw Cycles

Conclusions

1. Thin BASE discs were fabricated by tape casting and BASE tubes were successfully made by slip casting.
2. An electrochemical cell using $ZnCl_2$ electrodes showed that there is no increase in resistance, even after repeated cycling, suggesting that the BASE is stable in the atmosphere, and the proposed concept is viable.
3. Preliminary work shows that a complete cell could be assembled in the discharged state, and could be charged with a sodium anode.
4. Stability of BASE in an aqueous medium was demonstrated. This BASE has little affinity for water unlike the state-of-the-art BASE.
5. Electrochemical cells were successfully discharged.
6. Planar cells were assembled and tested to study the working of the same. From the voltage response it could be inferred that the planar cells can withstand several freeze-thaw cycles without any electrolyte failure.
7. The displacement reaction does not take place between $ZnCl_2$ and the BASE as there was no change in weight of the samples when treated with molten zinc chloride.